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NATIONAL BUREAU OF STANDARDS REPORT

9612

ANALYTICAL METHODS FOR MEASUREMENT OF TOXIC
COMPONENTS OF GASEOUS PRODUCTS IN FIRES --
A SURVEY

by

T. G. LEE



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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NATIONAL BUREAU OF STANDARDS REPORT

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421 6223

OCT 25 1967

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ABSTRACT

A survey was made of available methods of analyzing gases above 10 p.p.m. from fire involving polymeric materials. These included gas chromatography, specific ion electrode, colorimetric indicator tube, infrared absorption as well as some classical wet procedures. Experimental data on the accuracy of some indicator tubes, calibration techniques for gases in low concentrations and retention times of some components by a two-column chromatograph were also obtained. The limitations, estimated errors, interferences, and other pertinent data of the selected methods are summarized in the tables.

1. Introduction

This study was initiated to examine and develop methods of identifying the important chemical constituents of smoke and gases generated under fire conditions in modern dwellings. It considers the critical components of the gaseous products generated, and suggests effective methods and equipment suitable for both laboratory and field analysis. These methods were evaluated in terms of their desirable features, limitations, and reliability. The initial portion of the study on which this report is based, was confined to analysis of gases at concentration levels above 10 p.p.m. from fires with a high loading of polymeric materials.

In the past, considerable emphasis has been placed on achieving structural stability and low flammability as a means for providing safety during building fires. Recently, there has been increasing recognition of the life safety hazards associated with smokes and decomposition products formed during such fires. The justification for such emphasis seems evident when it is considered that, apart from fatalities caused by the direct ignition of clothing, smoke and toxic products were regarded as the major cause of death in fires during 1964, recorded by the fire brigades in the United Kingdom [1]. Before proposing code requirements to limit the hazard of smoke and gas during fires, it is desirable to have a detailed technical understanding of the materials and the effects of physical conditions under which these products are generated. Indispensable tools to permit such studies are reliable methods and techniques for analysis of the combustion products.

The problems of analysis of combustion products from polymeric materials in a fire are much more complex than in the case of cellulosic materials. Unlike fire gas studies of cellulosic materials in buildings [2] [3], studies of combustion products and their hazards from fire involving polymeric materials are limited. The analytical procedures and the toxicological effects of stable CO from cellulosic materials are rather well understood, whereas for example, the sampling problem of the very reactive HCl and physiological response to it have received but little attention in the literature [4]. It is interesting to note that hardwood under theoretical optimum burning conditions where all carbon is consumed and with CO and CO₂ in equilibrium at 700 °C, generates only 0.026 mole of CO per gram of wood. This compares with about 0.016 mole of HCl generated per gram of polyvinylchloride under any condition of combustion or pyrolysis at temperatures above 300 °C. But the estimated human tolerable limit for a few minutes is much higher for CO (3000 p.p.m.) than that for HCl (500 p.p.m.) [4,18]. Furthermore, experimental enclosure burning of cellulose-base fiberboard showed a maximum of about 0.017 mole CO per Gram [5]. On either of the above basis, combustion products of PVC appear to have greater potential hazard than those of wood. But the stability of the components are different and must be considered in evaluating this hazard. The CO remains airborne, whereas HCl, a highly reactive gas, combines rapidly with water vapor and, in this form or as pure gas, is rapidly adsorbed on walls or smoke particulate matter. This example shows the complexity of the problem and the need for basic studies.

2. Types of Gases and Vapors Expected and Their Significance

Thermal degradation studies of polymers [6] showed that as many as 30 distinct chemical components may result from decomposition and combustion of a given resin. In a fire where conditions may vary all the way from complete oxidation to low temperature pyrolysis and where numerous types of plastic materials are available, individual analyzable products may literally run into the hundreds. Some criteria are needed to minimize the number of components for which analyses must be made. For this purpose, the products may be divided into three categories: (1) Components which are likely to approach toxic concentration levels in a typical fire, (2) Components which give important clues to the rate and extent of burning, (3) Components which reveal the progress of an extinguishment effort. The significant ones in each category are as follows:

(1) Toxic Components	CO, HCl, HCN, NO ₂ , NO HF, HBr, Br ₂ , Cl ₂ , NH ₃ , SO ₂ , H ₂ S CO ₂ , COCl ₂
(2) Rate Components	O ₂ , CO ₂ , H ₂ O, N ₂ , CO
(3) Extinguishment Components	H ₂ O, CF ₃ Br, CF ₂ ClBr, CO ₂

The present discussion of analysis methods will be limited to these compounds only.

To obtain a reasonable characterization of a fire and its progress it may be necessary to monitor the concentration of only one or two components under each category. Obviously, the components selected depend on the type of combustible, location, and the time after the initial ignition. For example, at the ignition and growth state, the concentration of HCl and HCN from some plastic floor tiles, foam cushions, and furnishings in a typical room, can reach far above the toxic level in the vicinity of the source. But, due to its high reactivity and thus dropout rate, HCl may become quite negligible at some distance away from the source, or a short time after the source has ceased to burn actively. On the other hand, the rate of CO generation reaches its maximum during the later stages of burning. Because of its relatively slow decay rate, the concentration of CO slowly, but steadily, approaches some maximum value, and may far exceed a lethal level not only near the source, but at much greater distances away from it. Neglecting ventilation effects, this example shows the need for careful selection of both the sample probe location and the time of sampling for each gas in order to obtain meaningful results.

In general, it is desirable to minimize not only the number of analyses required, but also the amount of sample withdrawn for analysis, in order not to distort the combustion atmosphere. This is particularly true in smoke test chambers where the total volume may be relatively small.

3. Comparative Method of Analysis

The limitations, accuracy and some other pertinent data of two or more selected methods of analysis are presented in Table 1. In evaluating any particular method, the criteria of reliability, versatility, adaptability to automation, and availability from commercial sources of instrumentation are given emphasis at the expense of precision and a high degree of specificity. The table is self explanatory. The minimum value listed under the concentration range column means the minimum detectable concentration for the size of the sample indicated. In some

cases, however, a larger sample size may proportionally lower the detectable threshold. Conversely, smaller sample size or instrumental signal attenuation becomes necessary for components of higher concentration. Such flexibility applies mainly to the wet-chemical and gas chromatographic methods. Estimated errors (calibration) are errors expected from variation of individual indicator tubes (including reading) from the calibration based on representative samples of a given batch of tubes measured by the user. Under the analysis time column, the numbers denote the time interval before a second sample may be analyzed using the instrument for that particular component. More detailed discussion and experimental results will be given under the heading of each method.

3.1 Chromatography

The gas chromatographic technique is considered the most effective quantitative method for analysis of some components in fire gases. It requires a relatively small sample (1-5 cc), has good precision ($\pm 0.5\%$), wide dynamic range (10^4), and versatility. Though the method is not a continuous one, analysis time per sample of five components, excluding HCN, usually requires only about 15 minutes; with but little additional time for data reduction. However, this method is not useful for certain reactive components.

In the present application, an Aerograph 202-1B (Dual column and dual thermal conductivity detectors) chromatograph was used for the analysis of N_2 , O_2 , CO_2 , CO , H_2O , and HCN. Two columns, a 20' x 1/4" OD stainless steel column packed with 30-60 mesh molecular sieve 13x and a 6' x 1/4" OD Teflon column packed with 120-150 mesh Porapak R were arranged in series with a thermal conductivity detector at the end of each column. Fig. 1 shows a typical chromatogram and a schematic diagram of the flow system. The length of column packing, temperature and flow rate were chosen to avoid overlapping of the peaks. Air, CO_2 , H_2O and HCN were separated by the Porapak R while O_2 , N_2 , and CO were separated by the molecular sieve column. Helium was used as the carrier gas. Since the output polarity of the two detectors are opposite, manual or automatic switching of polarity is required if all output signals are to show as positive peaks. The minimum detectable limit was 30 p.p.m. for CO_2 , 200 p.p.m. for CO , 1000 p.p.m. for H_2O and 500 p.p.m. for HCN using a 1 cc sample with the peak area measured by a disc integrator coupled to the recorder. Larger samples would lower the limit proportionally. In practice, the sample is collected in the sampling valve in the chromatograph after sufficient flushing by vacuum. The tubing connecting the sample port and the valve consisted of a small diameter, 1/16 I.D. teflon tubing maintained at a temperature above that corresponding to the initial temperature of the gas sample, to avoid vapor condensation.

Though Hollis [7] and Obermiller [8] reported that HCl and H₂O may be separated either by a Porapak or a 5% Carbowax 200 column using either a stainless steel or teflon-coated thermal conductivity detector, such separation of HCl was not successful under the present operating conditions. Pretreatment of the column and detector with HCl were shown to be necessary. These modifications will be incorporated in future attempts to include HCl gas in the separations. Although HCl, reportedly, can be separated by the chromatographic technique, the minimum detectable limit is only 0.1% using a 5 cc sample [8]. Fish and coworkers reported the use of silica gel to separate fire gas components including HCl [9]. Other methods, notably the specific ion electrode, to be discussed later, appear much better suited for the determination of this component in the fire gases.

3.2 Colorimetric Indicator Tubes

The colorimetric indicator tubes used in this study were glass tubes 8 mm OD and of about 110 mm length available commercially in this country. They are packed with chemically impregnated granules which change color when the granules react chemically with a specific gas. A known volume of sample is drawn through the tube by a suction type hand pump located at one end of the tube. The concentration of the specific gas is indicated by the length of color change. Generally, there are layers of precleaning granules to adsorb interfering gases and a porous plug to control the sample flow rate. With good quality control during manufacturing and frequent calibration, some specific types of tubes can give useful results. In practice, however, there are several shortcomings:

1. Variation of packing density within the tube and non-uniformity of indicator gel among the tubes. Since sorption rate of sample gas by the gel depends primarily on the reacting surface area available per length of tube, variable density would affect reproducibility.
2. Unexpected interferences by certain gases and vapors not adsorbed by the precleaning layer which produce a color change similar to the gas of interest.
3. A gradual transition zone of the discolored stain front makes it difficult to judge the exact line of demarcation and thus introduces reading errors.
4. Gas sample temperature must be within a given limit, usually 0-40 °C to avoid errors.
5. Relative humidity of gas sample must be within a given limit for some tubes.

These shortcomings can be reduced in various way. For example, by frequent calibration to establish probable errors, by knowing the specific interfering gases in the sample and the sensitivity of the tube to these gases; and by determining the concentration of the interference gas, if any, by an independent method. With cumulative experience in using the tubes, both during calibration and sampling, the probable error in judging the line of demarcation of the colored section can be minimized. The merit of the colorimetric tubes, as in any other analytical method, should be judged by its performance on the problem at hand. Sensitivity, accuracy and interference depend on the chemical system used in the tube and they differ with different gases. Review of some of the techniques and problems associated with these tubes is given by Kusnetz, et al [10]. Table 2 shows indicating reagents used and interfering components of the tubes studied

The advantages of the indicator tubes are their convenience, simplicity, immediate results, and minimal sampling problem; with care they can produce reliable results. Tubes for analysis of HCl , HF , HCN and CO have been calibrated and examined for interference and temperature effect during this study.

Table 3 shows the calibration data for some of the colorimetric indicator tubes, the concentration ranges in which the tubes are applicable, the sample volume and rate in which the predetermined scale calibration (by manufacturer) holds. The length of the indicating layer compared with the maximum of the concentration range indicates the resolution of the tube. The transition zone is the width between complete color change and no change. It is a subjective estimate which determines the reading error. The value of indicated concentration was based on the mean of three separate determinations for each of the concentrations stated. Calibration procedures will be given in the next section. Unlike another study [10], where several disinterested observers were asked to judge the demarcation front of the color change, the present result was based on the observation of one individual. The calibration error for a pure, single mixture in air shows that both CO and HCN tubes showed an error within $\pm 20\%$, Type A HCl $\pm 20\%$, Type B HCl $+ 90\%$.

3.3 Calibration of Colorimetric Tubes

To avoid adsorption losses, low concentrations of HCl and HCN were prepared dynamically in a flow dilution system suggested by Saltzman [11]. Fig. 2 shows the schematic drawing of the arrangement. The system consists of an asbestos plug flowmeter [12] and a diluting tube. The

asbestos fiber was packed into a 1 mm I.D. teflon tube to impede the flow rate to a desirable range. The height of the liquid in the pressure regulating cylinder provided further control of the flow rate. The cylinder was filled with concentrated H_2SO_4 instead of water to avoid absorption of the metered gas by water. The asbestos plug flow meter was calibrated by attaching a graduated 0.1 cc pipet to the plug outlet and timing with a stopwatch, the movement of a drop of mercury past certain graduations. Flow rates as low as 0.01 cc/min can be achieved with stability and reproducibility. The degree of dilution of pure HCl from the tank was controlled by the asbestos plug flow meter and the diluting gas metered by a rotameter. Mixture concentration could be varied from 10 p.p.m. to 1000 p.p.m. A needle valve controlled the flow rate to the indicator tube. The pressure drop across the colorimetric indicator during calibration was balanced by applying an appropriate vacuum at the other end of the tube. This arrangement avoids creating any disturbance to the diluting system when the calibration starts with the insertion of the tube.

Low concentrations of HCN were generated by aeration of a 30 g per 100 cc solution of KCN in a midjet impinger. A thermostated water bath surrounding the bubbler maintained a temperature of 30 °C. The system produced an output of 100 p.p.m. Further dilution in the Saltzman apparatus was necessary for lower concentrations. Both the HCl and HCN systems were very stable and consistent.

A static method using a FEP teflon 5-mil-thick collapsible bag was used to generate low concentrations of other non-reacting gases. Under this arrangement, the sample gas was introduced into the bag by a gas-tight microsyringe and diluted with air or other gases from a one liter syringe. This method is not applicable to HCl or HCN because of losses resulting from adsorption by the bag surfaces but gave satisfactory results with CO from 10 to 1000 p.p.m.

3.4 Specific Ion Electrode

A permeable membrane electrode designed by Pungor for chloride ions, available recently [13], was used in a system to determine HCl concentrations in the gas sample, potentiometrically. This method has higher accuracy, range, and reliability than that of the colorimetric indicator tube. Its working range for a 100 cc gas sample is between 20 and 20,000 p.p.m. For lower concentrations, a larger sample must be used. Specific Ion Electrodes for Chloride, Fluoride and Bromide available from Orion Research Inc. were also used.

In practice, the highly soluble HCl gas and vapor in the sample (100 cc) was totally absorbed by water when the sample flowed at a rate of about 100 cc/min through a long narrow spiral passage of a threaded Teflon plug covered by a water-saturated paper inside a glass tube. Whatman No. 2 filter paper, as described in Fig. 3, wetted with 0.1 cc water was used. An alternative method is the use of about 40 mg of glass wool as a filter in a 1/4 OD Teflon tube. The glass wool was also wetted with 0.1 cc of water. The exposed paper or wool was carefully transferred to a Teflon cup of small internal volume. Water was added to make a total solution of 1 cc before insertion of the specific ion electrode and a low leakage, small-diameter-tip, conventional calomel KCl reference electrode (Beckman 39270). A high impedance, differential voltmeter or an expanded-scale pH meter may be used to measure the EMF between the electrodes. The specific ion electrode has a sensitivity limit in the order of 1×10^{-5} mole/liter for chloride ions in solution and a equilibrium response time of about 1 min. It consists essentially of polymeric silicone rubber membrane impregnated with particles of silver chloride precipitate. The membrane covers the tip of a small diameter glass tube filled with a chloride solution. Fig. 4 shows the calibration curve of potential in mV versus HCl concentration in p.p.m. calculated on the basis of 100 cc sample absorbed in a 1 cc water. The curves were based on measurement made with solutions of known HCl concentration.

Known interference of Br or I ion on the chloride electrode is reported to be negligible if the concentration of these ions are less than 0.1 that of the chloride ions [13]. Fluoride ion concentrations less than 10 times that of the chloride ions produce no interference. In most fire gas or smoke chamber analyses, this problem would not arise. In cases where bromide ion concentration is expected to exist in the same order as that of chloride, a bromide specific ion electrode can be used. This electrode is not affected by chloride ions at concentrations as high as 50 times that of the bromide ions. A fluoride ion electrode, with a sensitivity as low as 10^{-6} moles/liter is a preferred instrument for HF concentration measurement. The latter electrode shows no interference from other halogen ions if their concentration are less than 10,000 times that of the fluoride ions [19].

3.5 Infrared Methods

In certain cases where continuous monitoring of a single component in a multi-component sample is essential, non-dispersive infrared methods may be used [14][15]. Such instruments are commercially available from the Mine Safety Appliance Company and Beckman Instrument Company. The

analysis is based on the difference of absorption of infrared radiation between a reference and a sample cell, the detector being sensitive to a single gas. For the MSA instrument, a nominal range of 0-2000 p.p.m. for CO and CO₂; 0-3000 p.p.m. for NH₃; and 0-5000 p.p.m. for SO₂ with an accuracy of $\pm 2\%$ of full scale is available. Detectors for some other gases are available at about the same sensitivity. Flow rates in the order of 1000 cc/min are required for continuous analysis. Several specific detectors may be connected to monitor other components in the sample. The specificity of the method depends on knowing other major components in the sample whose spectra may possibly overlap those of the component of interest. Discrimination ratio values predicting the degree of interference among some gases are available for feasibility studies [16].

Though considered a non-continuous method, a regular dispersive infrared spectrophotometer equipped with special gas cells may also be used to measure gas components in the low concentration range. The method is only suited for samples with a low number of major components which would avoid the difficulty of excessive overlapping of spectra. Unlike the non-dispersive method, however, the display of the complete spectrum helps identify and gives quantitative information on all components of the sample. The sensitivity expressed as a minimum detectable concentration, using a simple 10 cm-path-length gas cell (sample volume 200 cc) is shown on Table 4 [17]. For a smaller sample and higher sensitivity, micro gas cells may be used. These are multi-path cells with an internal reflecting mirror to increase the path length. A 60 cm path length (sample volume 22 cc) cell is available from Beckman Instrument Company. The six-fold improvement in sensitivity of detectable concentration over that shown in Table 4 would make the cell useful for HCN, NO₂ and CF₂Br Cl. A longer path length cell such as the 10 meter cell (sample volume 4000 cc) may also be useful under some situations. Corrosive gases may be harmful however, to mirrors in multi-path cells.

Except for the continuous analysis of CO and CO₂ using the non-dispersive IR and the measurement of HCN using the 10 cm cell in the dispersive IR instrument, infrared methods in general do not appear to be particularly suited for the analysis of other components in fire gases as compared with other available methods.

4. Summary

This report has examined some of the quantitative analytical methods of analyzing fire gases resulting from combustion of plastic materials. It points out the significant limitations as well as advantages of some of the basic analytical methods. Tables are presented to show pertinent data on two methods considered to be well suited for laboratory and field use in the analysis of about 15 gaseous components. Although the gas chromatographic and specific ion electrode techniques are invaluable, the necessity for classical wet methods, in some cases, still exists. The sampling technique, involving smoke particles, aerosols and gas phase needs considerable study because of the way individual components can partition among the three phases. Reliable results must be based on recognition of this fact.

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TABLE 1 SUGGESTED METHODS OF FIRE GAS ANALYSIS

Gas	Method C=Continuous B=Batch	Useful Concentration Range	Estimated Error	Sample Size		Analysis Time min	Inter- ference	Remarks
				Volume cc	Flow cc/min			
N ₂	Chrom. Molecular Sieve (B)	0.1 - 100	± 0.5	1		5	0	
O ₂	Chrom. Molecular Sieve (B)	0.1 - 100	± 0.5	1		4	0	
	Magnetic Susceptibility (C)	0.02- 20	± 2		1000			60 sec response
CO ₂	Chrom. Porapak (B)	30- 10 ⁶	± 0.5	1		3	0	
	Infrared, Nondisp. (C)	20-2000	± 2		1000		P	30 sec response
H ₂ O	Chrom. Porapak (B)	0.1 - 7	± 2	1		12	0	
CO	Chrom. Molecular Sieve (B)	200- 10 ⁶	± 0.5	1		9	0	
	Infrared, Nondisp. (C)	20-2000	± 2		1000		P	30 sec response
	Indicator Tube (B)	10-3000	± 20*	100-1000		1-2	P	
HCN	Chrom. Porapak (B)	500- 10 ⁶	± 0.5	1		24	0	
	Infrared, 10 cm cell (B)	30- 10 ⁶	± 2	200		7	P	at 14.1μ
	Indicator Tube (B)	2- 150	± 20*	100- 500		1	P	
HCl	Indicator Tube (B)	2- 300	± 20*	100-1000		1	P	Sensitivity range of ions in solu- tion 10 ⁻⁵ -10 ⁻¹ mole/l
	Absorp. Ion Electrode (B)	10-5000	± 10	100		3		
HF	Indicator Tube (B)	0.5- 15	± 20*	1000		1	P	
	Absorp., Ion Electrode (B)	5-1000	± 10	100		3	O	10 ⁻⁶ -10 ⁻¹ mole/l
HBr	Absorp., Turbidimetric (B)	10-2000	± 5	100			P	
	Absorp., Ion Electrode (B)	5-1000	± 10	100		3	P	10 ⁻⁶ -10 ⁻¹ mole/l

TABLE 1 SUGGESTED METHODS OF FIRE GAS ANALYSIS

Page 2

Gas	Method C=Continuous B=Batch	Useful Concentration		Estimated Error	Sample Size		Analysis Time	Inter ference	Remarks
		%	Range		Volume cc	Flow cc/min			
Cl ₂	Indicator Tube (B)		0.2- 30	---	100-1000		1	P	Liberation of
	Absorp., Colorimetric (B)		1-2000	± 5	1000		3	P	I ₂ from KI colorimetric
NH ₃	Infrared, Nondisp. (C)		30-3000	± 2		1000		P	Interference
	Indicator Tube (B)		25-7000	---	100-1000		1	P	by amines
SO ₂	Absorp., Colorimetric (B)		2-2000	± 5	1000		3	P	Fuchsin Fomalde
	Indicator Tube (B)		10-1500	---	100-1000		1	P	hyde method
COCl ₂	Indicator Tube (B)		0.5- 75	---	100- 500		1	P	
	Absorp., Iodometric		2-2000	± 5	1000			P	2% NaI in Acetone
CF ₃ Br	Chrom. Carbowax 20M (B)		10- 10 ⁶	± 0.5	1		10	O	
CF ₂ ClBr	Chrom. Carbowax 20M (B)		10- 10 ⁶	± 0.5	1		10	O	
	Infrared 10 cm cell (B)		100-5000	± 2	200		7	P	at 11.5 μ

* For the limited number of tubes in each batch studied, the standard deviation was found to be within ±20%.
 Calibrations based on known concentrations were found to differ from manufacturer's calibration by as much as 90%.
 See Table 3. User calibration of different batches is necessary to establish error.

Abbreviation:

Chrom. - Gas Chromatography
 Nondisp. - Nondispersive

Ion Electrode - Specific Ion Electrode

Absorp. - Absorption by a liquid followed by other analysis

P - Interference possible, by other components

O - No Known Interference

TABLE 2. INTERFERING COMPONENTS ON COLORIMETRIC TUBES

Nominal Conc. Range ppm	Indicating Reagents	Interfering Components	Non-Interference
Tube			
**HCl Type A	Organic Metal Salt to react with Cl	H ₂ S > 20 ppm, no HCl sensitivity. (Cl ₂ , NO ₂ , NO) ≥ HCl, reading will be low HF > 3 x HCl, reading will be high H ₂ O > 70% RH, reading will be low H ₂ O < 30% RH, reading will be high	HCN, CO, SO ₂ , SO ₃
HCl Type B	Congo red on beaded alkali salt	Any strong acid gas	
**HCN	Hg salt to release acid gas	H ₂ O > 90% RH NO ₂ > 50 ppm NH ₃ > 1000 ppm HCl > 5000 H ₂ S > 300 CO > 5000 SO ₂ > 200 Other acid gases in high concentrations (above adsorption limit of precleaning layer)	
**CO	Iodine Pentoxide Selenious Dioxide Sulfuric Acid	Saturated and unsaturated Hydrocarbons > 4000 ppm Hydrocarbons to CO ratio > 30.	H ₂ O, HCl, and HCN adsorbed by precleaning layers (Watch precleaning layer saturation by color change)
NH ₃	Gold Chloride	Aliphatic Amines H ₂ S > 50 ppm	Hydrocarbons
HF	Alizarin-Zirconium Complex	None known Specific for HF	HCl, SO ₂ , NO ₂ , CO
NO+NO ₂	Diphenylbenzidine	$\frac{\text{HCl}}{\text{NO}_2} > 270$ $\frac{\text{Cl}_2}{\text{NO}_2} > 2$	
SO ₂	Iodate	Reducing Compounds	

* Data based on manufacturer's information.

** The lack of mutual interference among HCl, HCN and CO for these tubes for concentration up to 1000 ppm HCl, 100 ppm HCN and 1000 ppm CO was confirmed by NBS results.

TABLE 3 . COLORIMETRIC INDICATOR TUBES

Basic Data (supplied by Mfr.)				Calibration Data (NBS)					
Tube	Concentration Sample		Sampling Rate sec/stroke	Packing Length		Transition Zone		Concentration	
	Range ppm	Volume cc		Precleaning mm	Indicating mm	Length mm	Error %	Actual ppm	Indicated ppm
HCl Type A	2- 30	1000	11	30	60	4	±7	5	30
	10- 300*	100						25	30
								86	95
HCl Type B	2- 100	500	30	0	65	2	±3	300	570
	20- 500	100							
CO	10- 300	1000	27	40	50	2	±4	50	120
	100-3000	100						100	220
								200	500
HCN	2- 30	500	10	30	50	6	±8	5	35
	10- 150	100						30	
								75	
HF	1- 15	1000	5	0	60	3	±5	16	14
	5- 150*	100							
NO + NO ₂	0.5-10	500	9	30	60	5	±8		
	5- 50*	100							
SO ₂	5- 150	1000	12	0	65	4	±6		
	50-1500	100							
NH ₃	25- 700	1000	9	0	75	3	±4		

* Concentration range extended by use of individual calibration (not furnished by the manufacturer)

‡ Average readings of three separate tubes

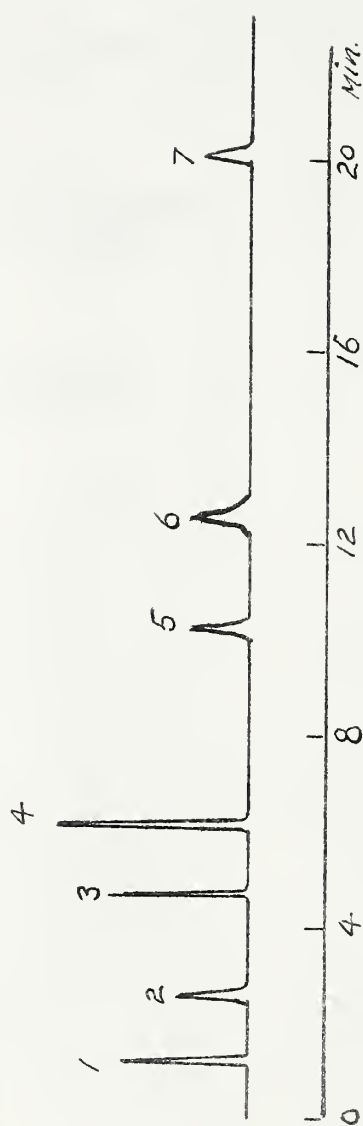
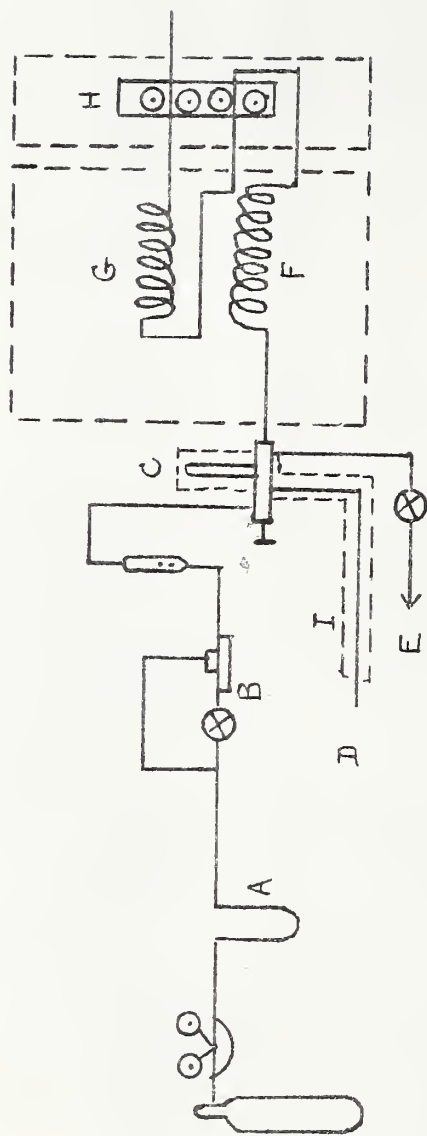
TABLE 4 MINIMUM DETECTABLE CONCENTRATION

Using a 10 cm cell*

<u>GAS</u>	<u>CONCENTRATION</u> ppm	<u>PEAK WAVE LENGTH</u> μ
CO ₂	300	4.3
CO	1,000	4.6
HCN	30	14.1
HCl	10,000	3.4
NH ₃	300	10.3, 10.8
NO ₂	100	6.2
SO ₂	300	7.3
NO	3,000	5.2
HBr	30,000	3.9
CF ₃ Br	30,000	8.3
CF ₂ BrCl	100	11.5

* See reference [17]

- A - Mol. Sieve Trap
- B - Differential flow controller
- C - Sampling valve
- D - To Sample Source
- E - Vacuum
- F - Porapak Column
- G - Mol. Sieve Column
- H - T. C. Detector
- I - Wrap-on Heater



- | | | |
|----|------------------|--------------|
| 1. | Air | 1st detector |
| 2. | CO ₂ | " " |
| 3. | O ₂ | 2nd " " |
| 4. | N ₂ | " " |
| 5. | CO | " " |
| 6. | H ₂ O | 1st " " |
| 7. | HCN | " " |

Conditions: Column 6' x 1/4" Porapak R and 20' x 1/4" Mol. Sieve 13 x
 Temp: Column 75 °C Det. 105 °C
 Flow: 60 cc/min He
 Sample: 1 cc

Fig. 1. Chromatogram of Some Combustion Products and Schematic Diagram of the Apparatus

Figure 2 Flow Dilution and Calibration Arrangement

- | | |
|----------------------------|----------------------|
| 1. Gas of interest | 5. Diluting gas |
| 2. Pressure regulator | 6. Mixture waste |
| 3. Asbestos plug flowmeter | 7. Colorimetric tube |
| 4. Rotameter | 8. Vacuum source |

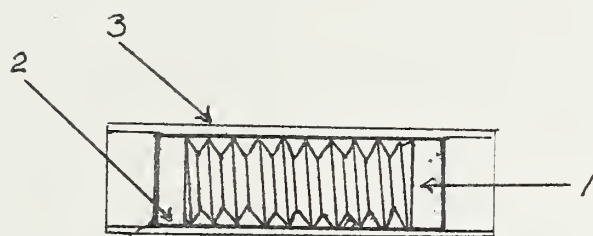
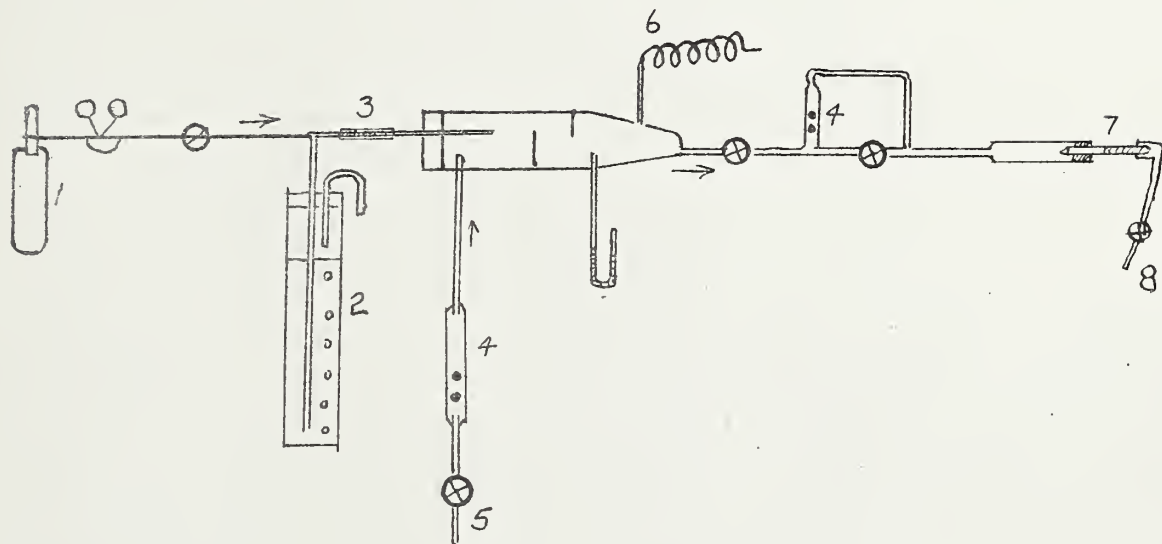


Figure 3 Sample Gas Absorption Device

1. Teflon rod, 1 1/4" x 1/4" O.D., threaded with 1/4 - 20 N.C. threads.
2. No. 2 filter paper, 1" x 0.78".
3. Glass tubing, 1 1/2" x 0.247 I.D.

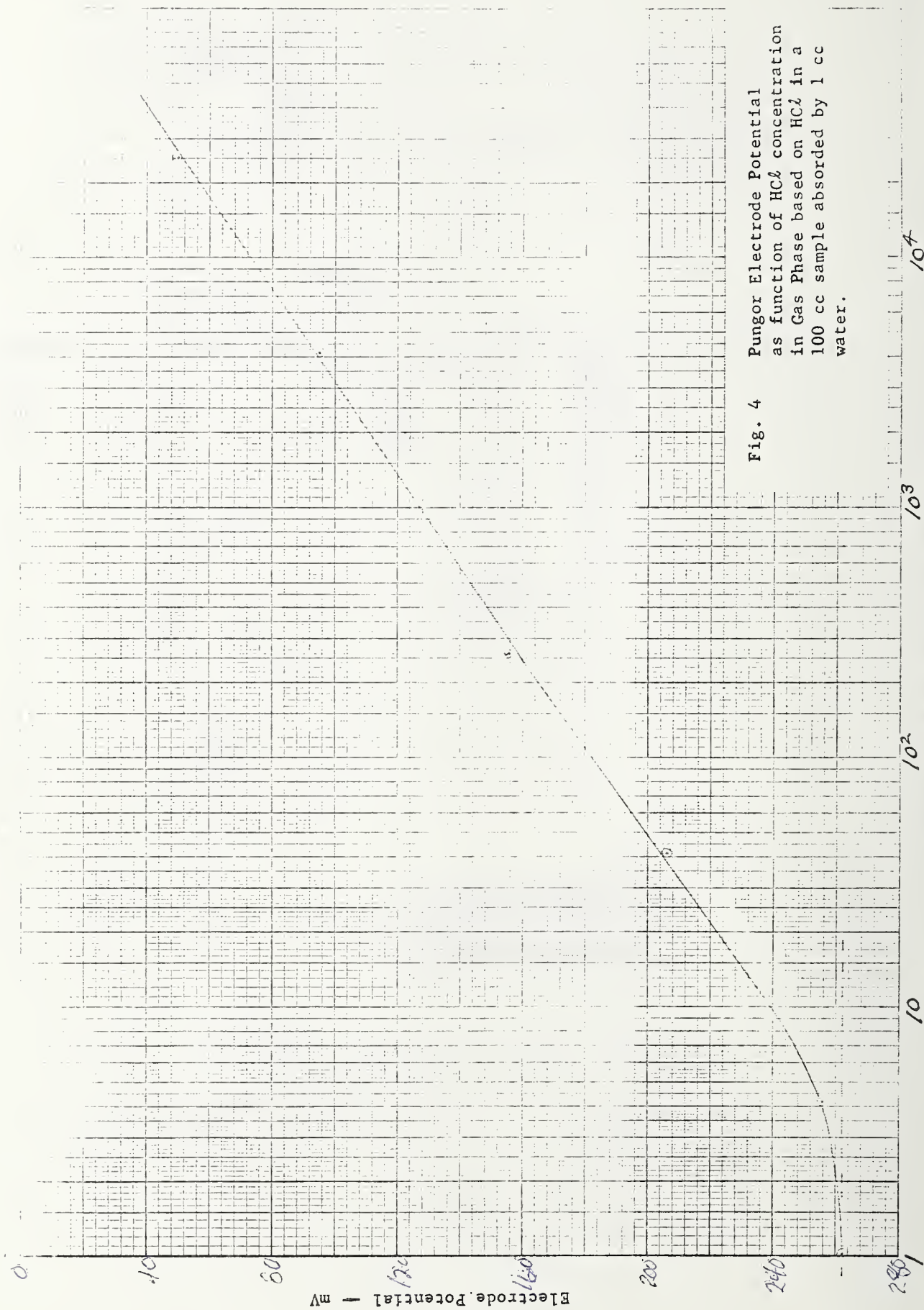


Fig. 4 Pungor Electrode Potential as function of HCl concentration in Gas Phase based on HCl in a 100 cc sample absorbed by 1 cc water.

Concentration of Gas Phase HCl — P.P.N.

